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(51) INT CL⁴

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C2C CAA CMB C1510 C215 C22Y C220 C226 C246
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C634 C652 C666 C672 C699 C80Y C815 C821
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U1S S1346 S1387 S1424

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None

(58) Field of search

UK CL (Edition J) C2C CBL CMB CMC CNR
CAS Online

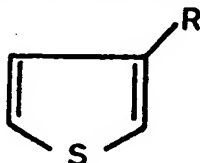
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(54) Thiophene monomers and polymers prepared therefrom

(57) A novel monomer having the general formula



where R is certain specified substituent groups, can be polymerised to form conducting polymers which possess liquid crystal properties. A particular example of such a compound is 4-cyano-4'-(3-thienyl-methoxy)biphenyl.

U S 2 2 2 5 0 0 8 A

FIG. 1.

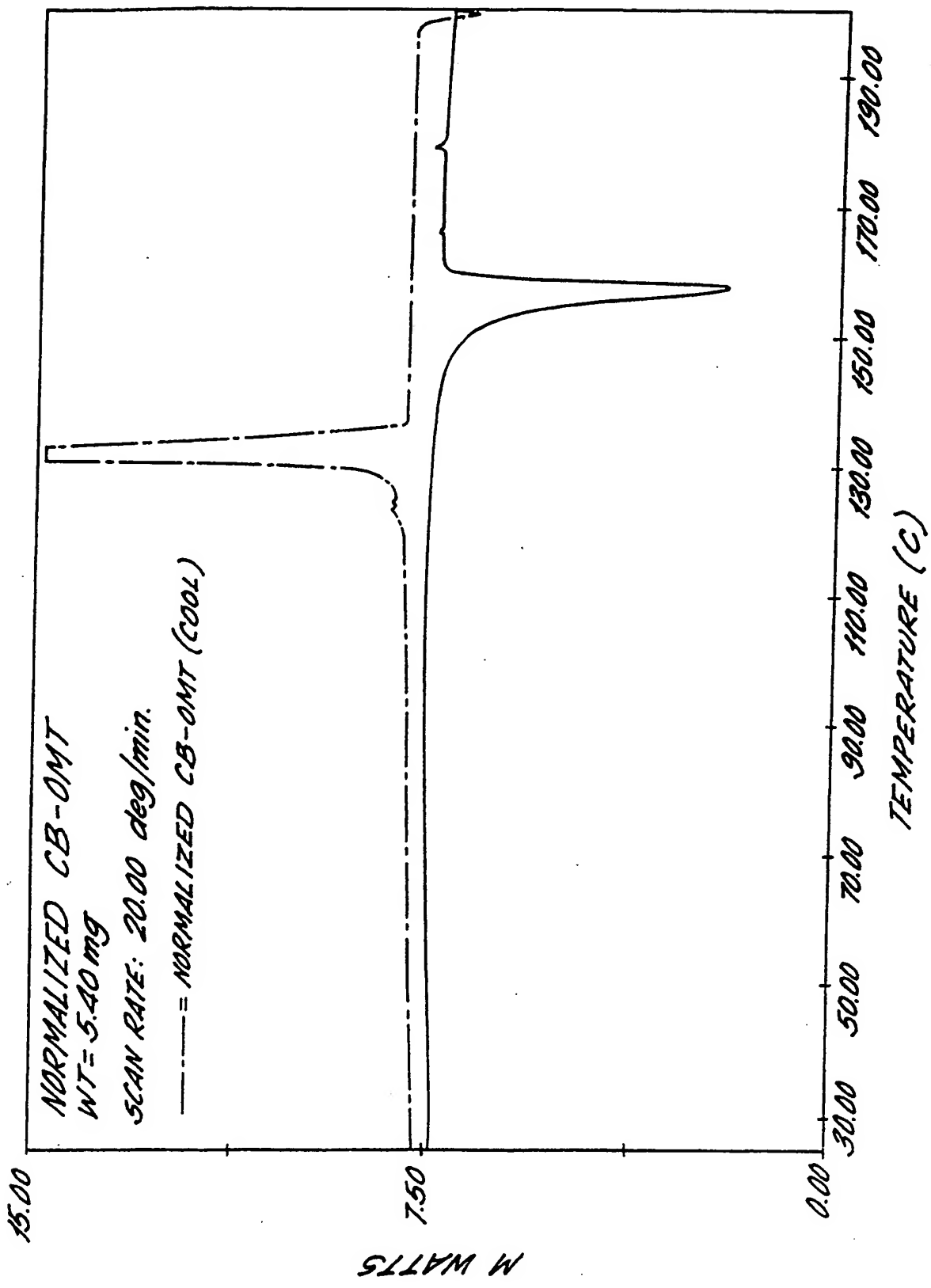
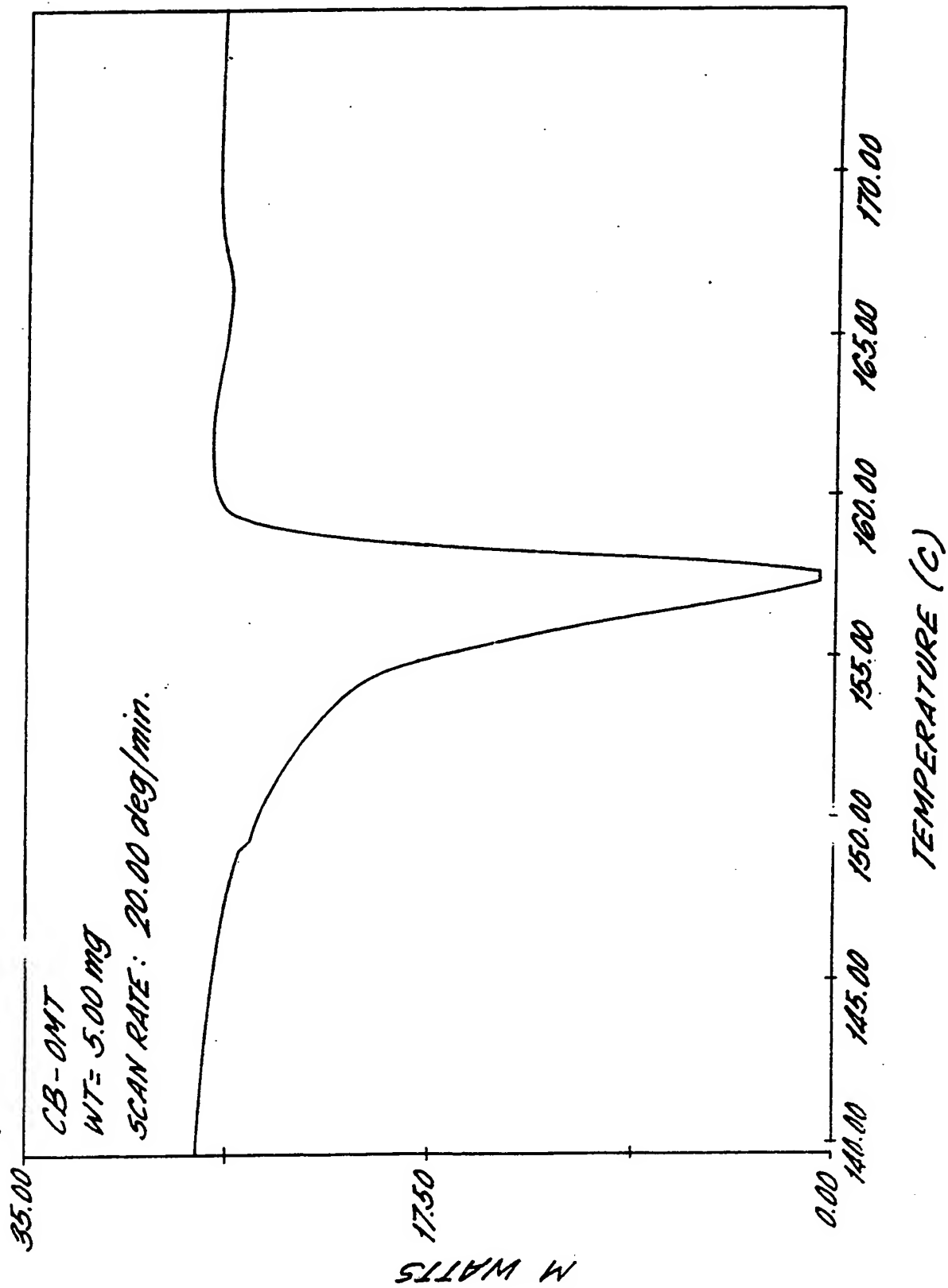
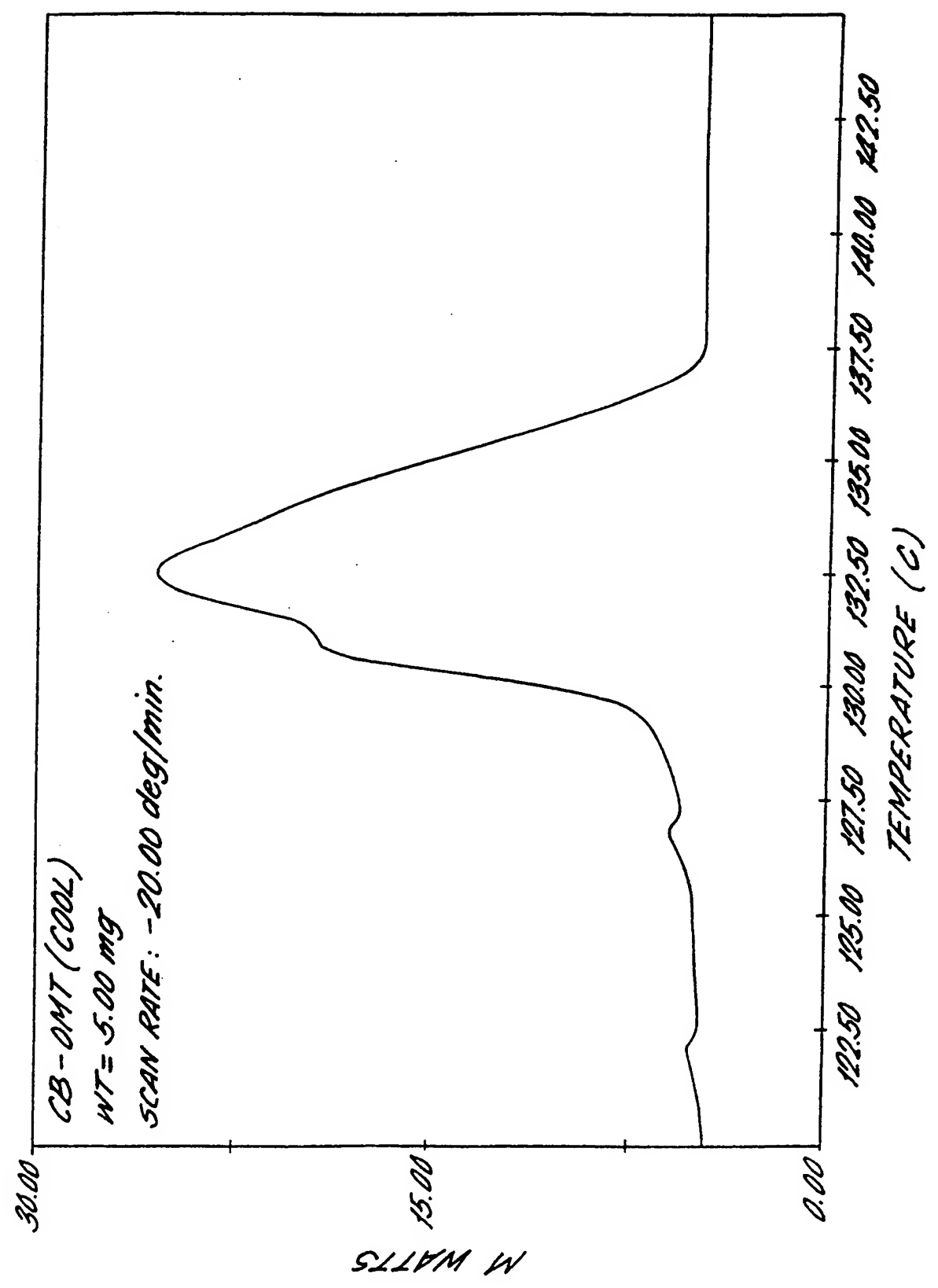


FIG. 2a.



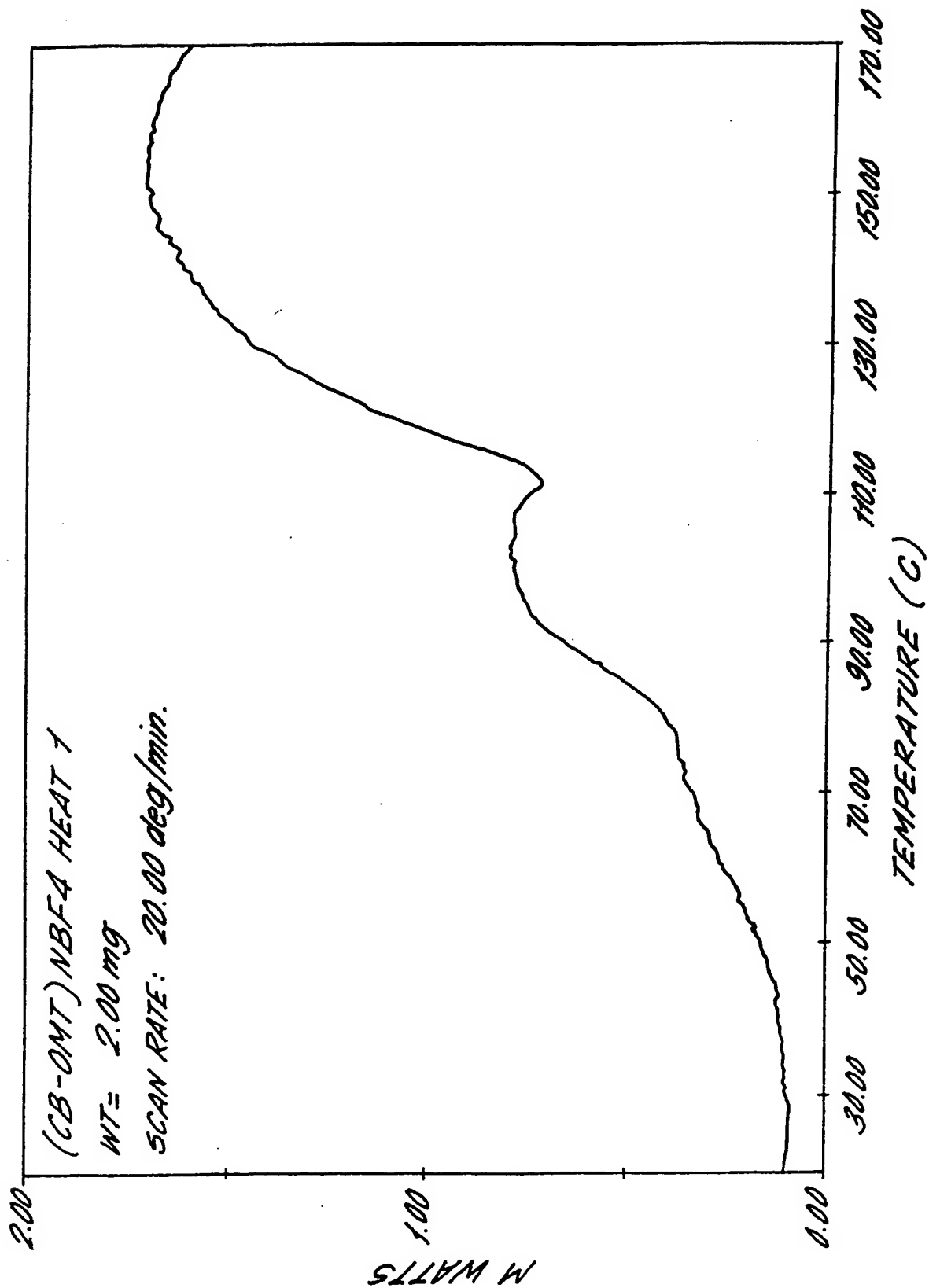
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FIG. 2b.



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FIG. 3a.



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FIG. 3b.

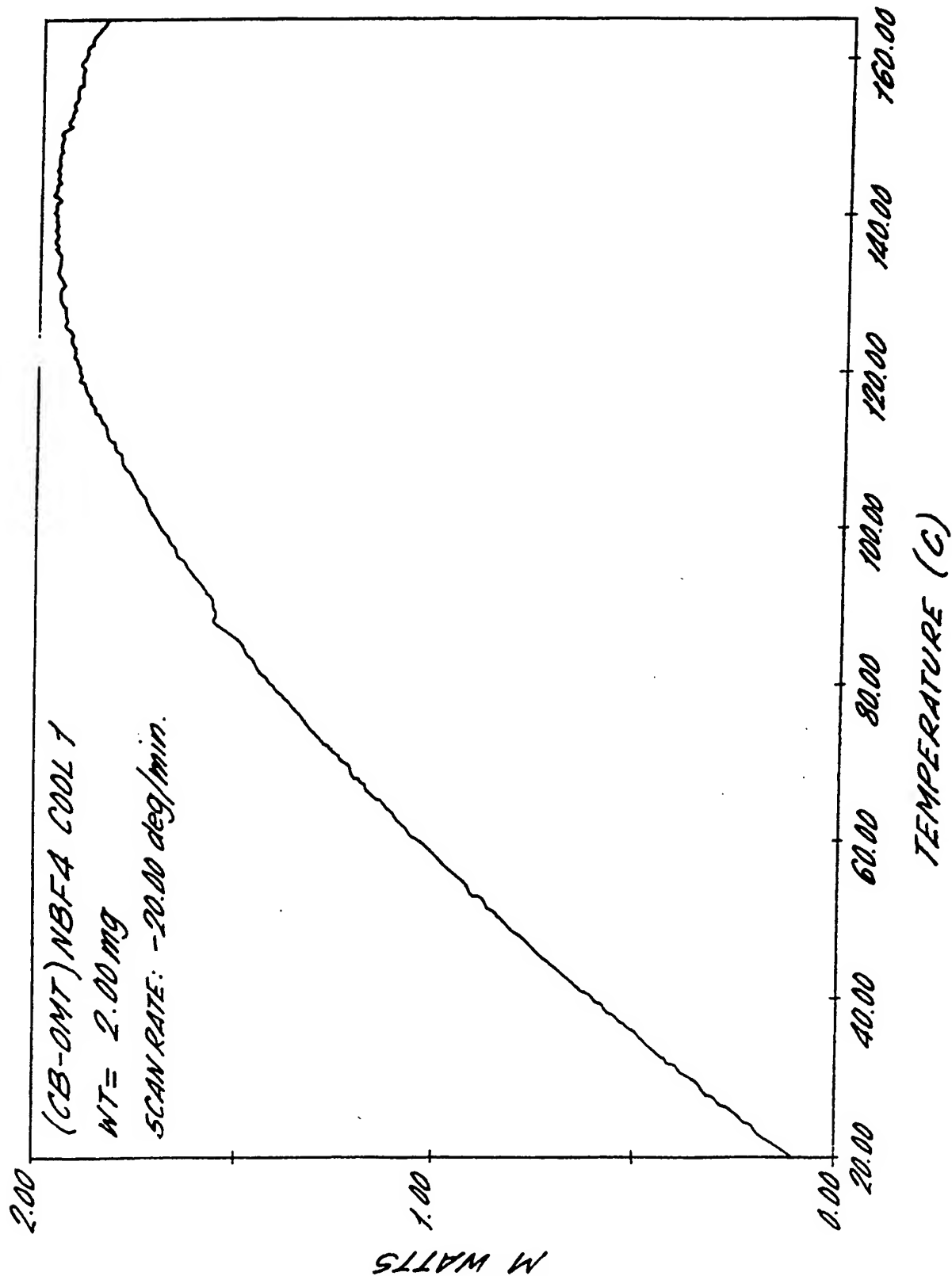
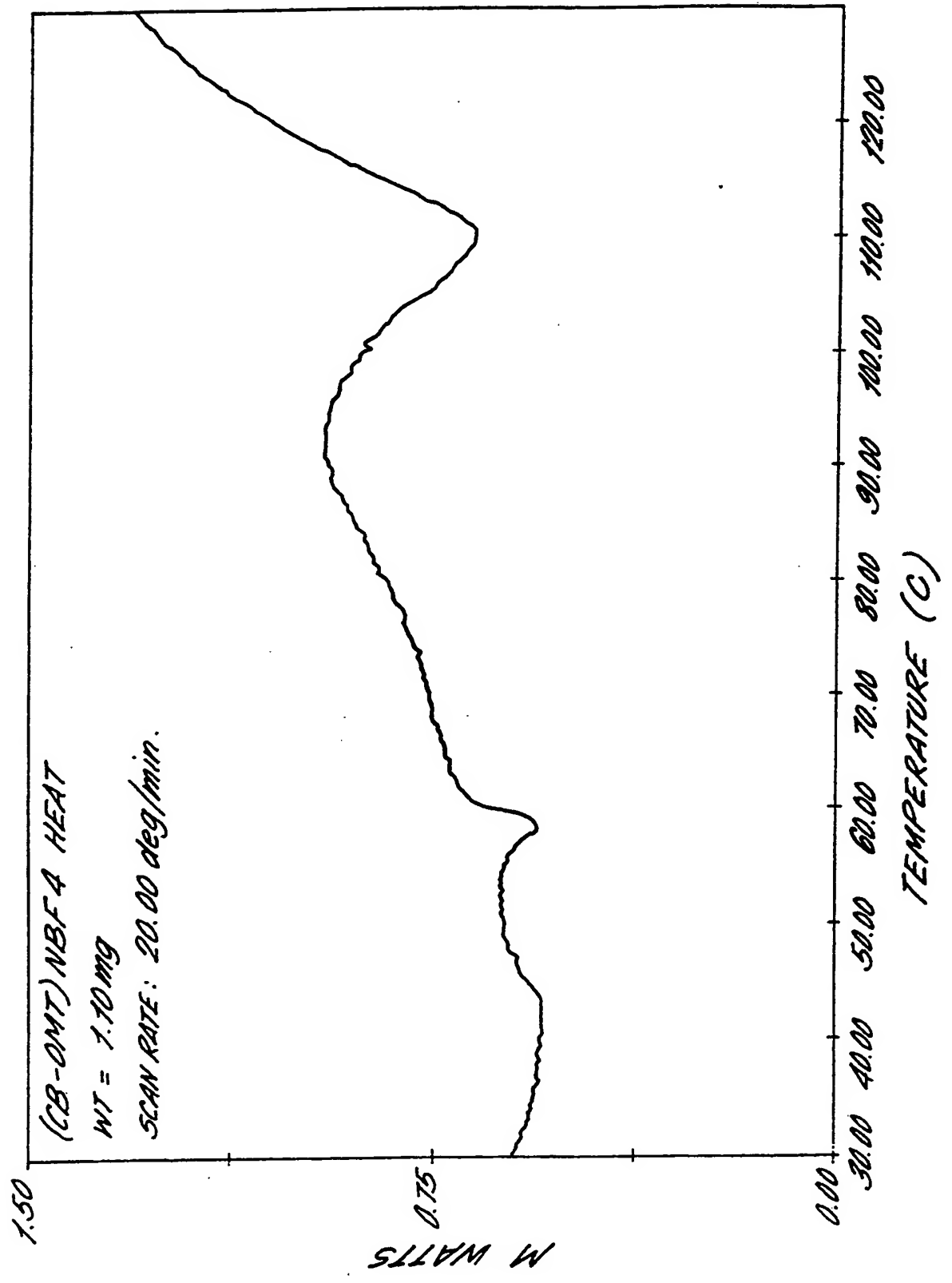
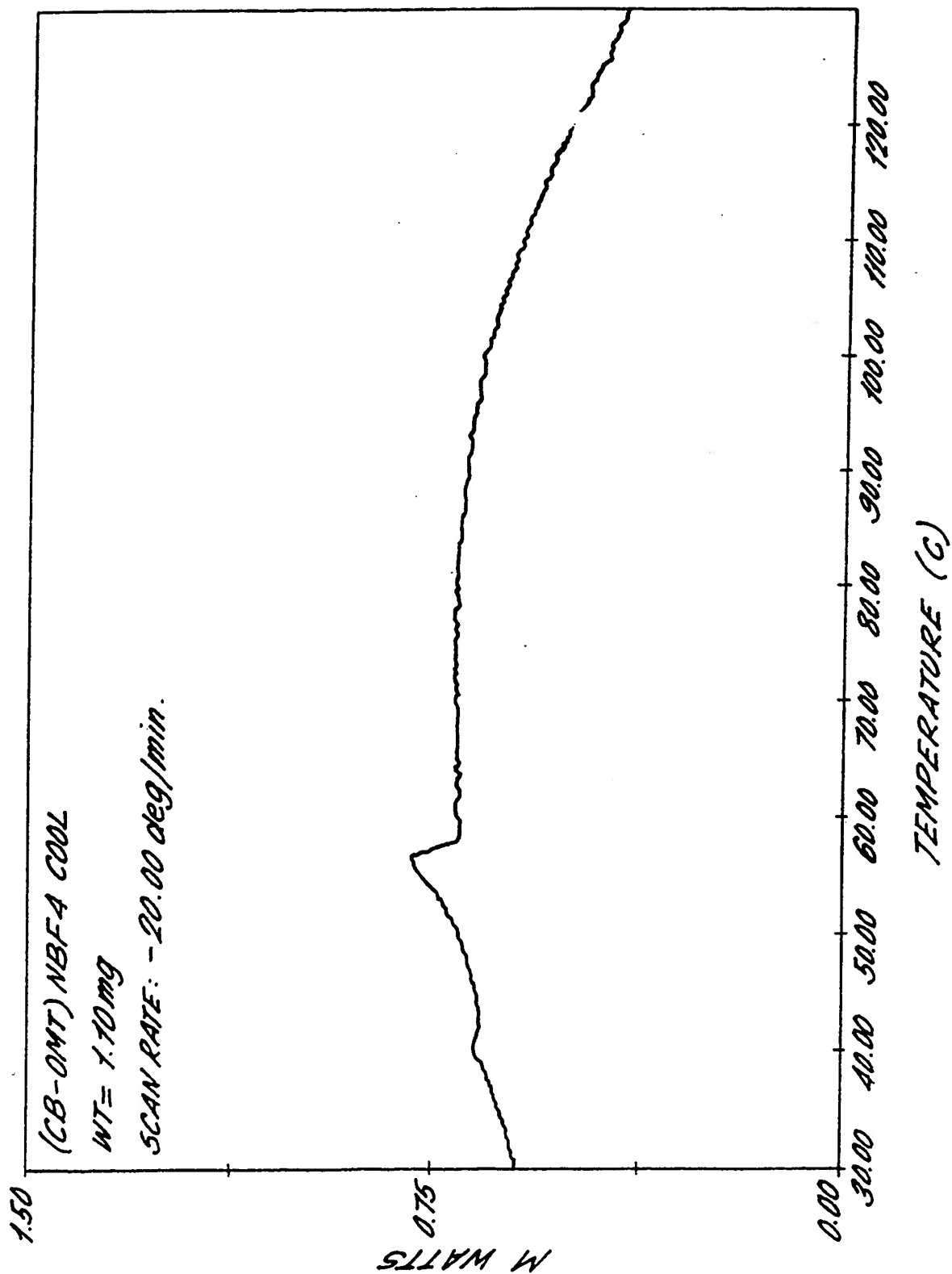


FIG. 4a.



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FIG. 4b.



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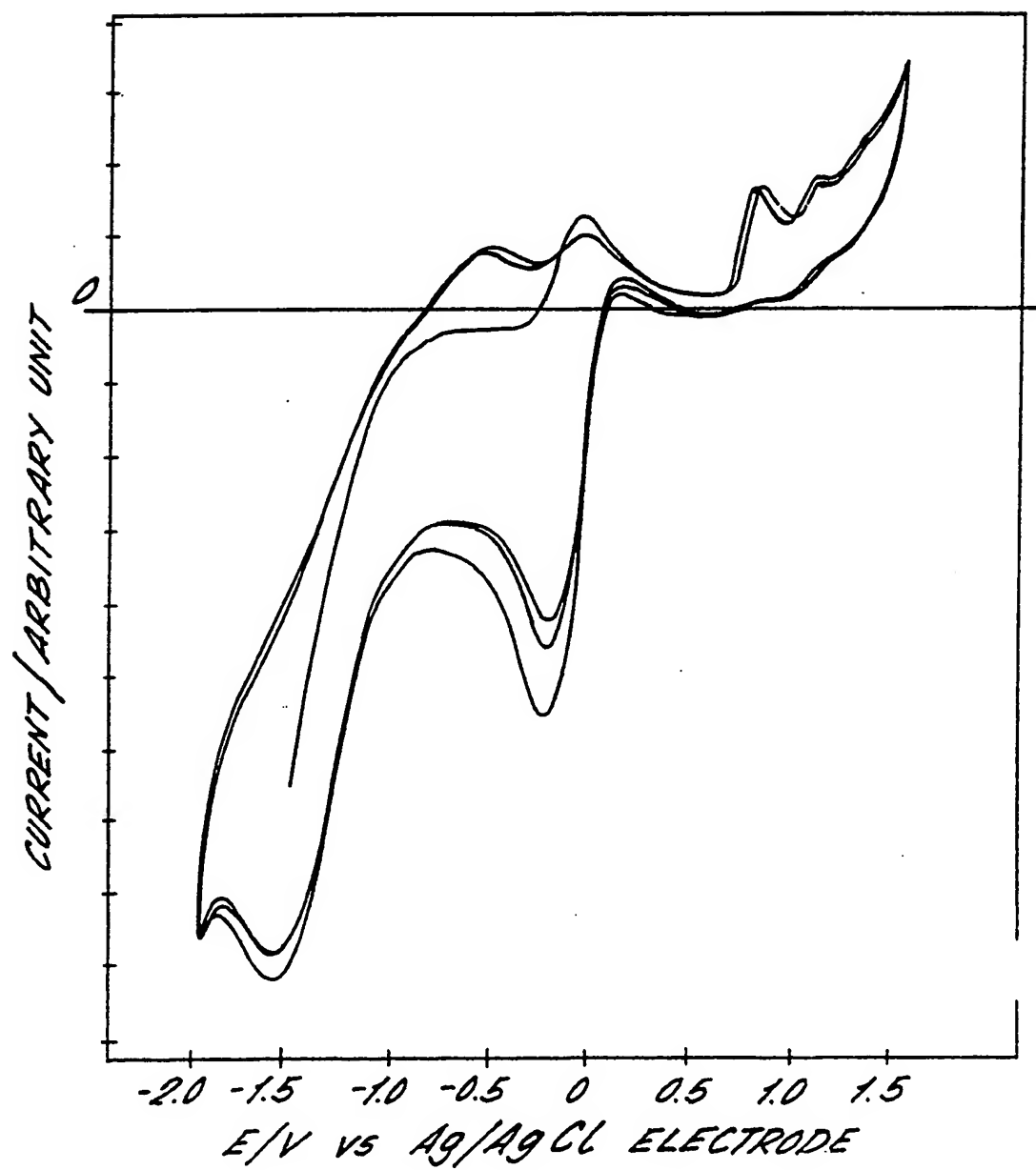
FIG. 5.

CB-OMT = 5mm

$\text{Bu}_4\text{N}^+\text{ClO}_4^- = 0.5\text{ M}$

SOLVENT = ACETONITRILE

ELECTRODE = Pt.



THIOPHENE MONOMERS AND POLYMERS
PREPARED THEREFROM

The present invention relates to certain novel
 5 thiophene monomers and to electrically conducting
 polymers which are prepared therefrom.

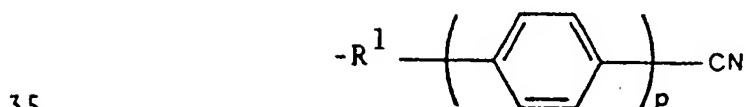
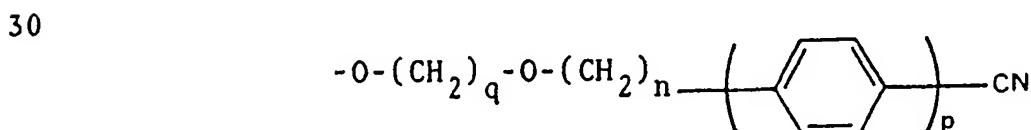
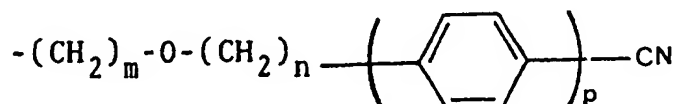
The Journal of the Chemical Society, Chemical
 Communications, 1986, pages 1346 and 1347, Kwan-Yue,
 G.G. Miller and Ronald L. Elsenbaumer, discloses
 10 homopolymers and copolymers of 3-alkylthiophenes,
 such as 3-ethyl, 3-n-butyl-, 3-n-octyl and
 3,4-dimethylthiophene.

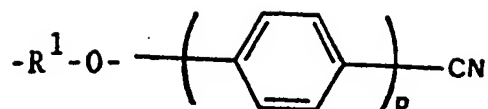
We have now discovered certain novel substituted
 thiophenes which can be polymerised to form
 15 conducting polymers which possess liquid crystal
 properties.

Accordingly, the present invention provides a
 compound having the general formula:

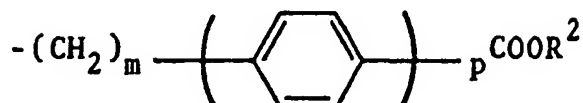


25
 wherein R is





5



R^1 is a straight or branched chain alkylene group containing from 1 to 8 carbon atoms;

10 R^2 is a phenyl group substituted with a cyano group or an alkoxy group containing from 1 to 6 carbon atoms;

n is 0 or an integer of from 1 to 6;

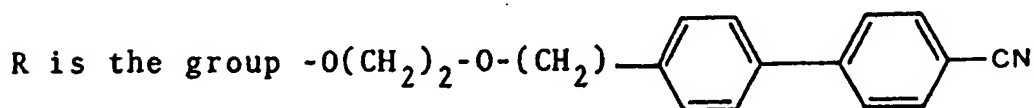
15 m is 0 or an integer of from 1 to 6;

p is an integer of from 1 to 3;

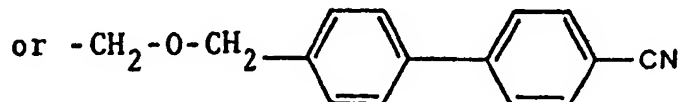
q is an integer of from 1 to 6.

Preferred thiophene monomers are those in which

20



25

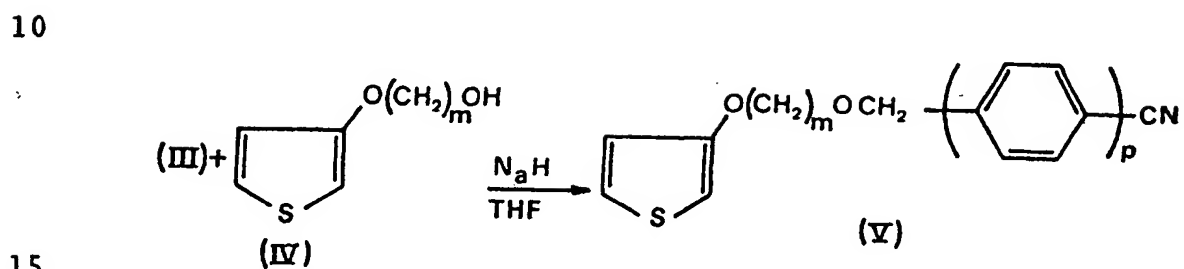
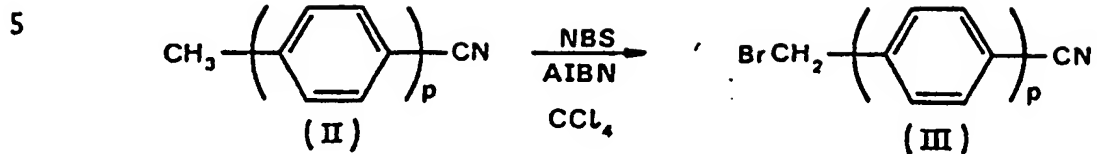


The thiophenes of the present invention may be synthesised according to the following reaction schemes:-

30

35

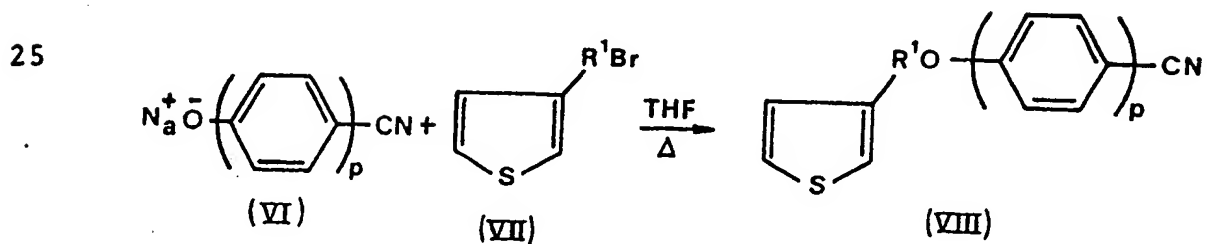
Scheme 1



NBS = N-bromosuccinimide

AIBN = azobisisobutyronitrile

Scheme 2



The other compounds of the present invention may be prepared using variations of these reaction schemes.

5 The thiophene derivatives of the present invention can be polymerised, for example using an electrochemical polymerization process, to provide electroconductive polymers.

10 The present invention includes within its scope a process for the preparation of a polythiophene derivative which process comprises subjecting a thiophene monomer as above defined in a non-aqueous solvent to electrochemical oxidation at an electrode potential which is at least as electropositive as the oxidation potential of the thiophene monomer.

15 The electrochemical polymerization of the monomers of the invention may be carried out, for example, in a single compartment cell using an anode of platinum, indium-tin oxide (ITO), tungsten, titanium, niobium, nickel, lead or graphite.

20 The thiophene derivatives of the present invention exhibit liquid crystal properties and thus are of potential use either alone, or when mixed with other compounds which exhibit liquid crystal properties, in liquid crystal applications.

25 The present invention furthermore includes within its scope a polythiophene derivative which comprises repeating units of the general formula:



wherein R is as defined above, and counterions of the formula X, where X is chloride, bromide, sulphate, bisulphate, nitrate, tetrafluoroborate, alkylsulphonate, arylsulphonate, arenecarboxylate,

35

alkylcarboxylate, arenedicarboxylate, polystyrene-sulphonate, polyacrylate, cellulose sulphonate, cellulose sulphate, polyamic carboxylate, H_2PO_3^- , H_2PO_4^- , PF_6^- , SbF_6^- ,
5 AsF_6^- or a perfluorinated polyanion.

Examples of arylsulphonates are p-toluenesulphonate, benzenesulphonate, 9,10-anthraquinonesulphonate and anthracene-sulphonate, an example of an arenedicarboxylate is
10 phthalate, whilst an example of arenecarboxylate is benzoate.

The electrolyte is chosen so as to provide the counterions as above defined.

The solvent is preferably acetonitrile,
15 dichloromethane, chloroform, nitromethane, dichloroethane, nitrobenzene, propylene carbonate, N-methylpyrrolidone, sulpholane, dimethylformamide or dimethylsulphoxide. The solvent may be used alone or as a mixture of two or more thereof.

20 The thiophene polymers of the present invention are conductive and therefore may be used in thin film technology, as EMI/RF shielding materials, as antistatics, in electrochromic display systems, as ion and pH sensors, as gas sensors, as battery
25 electrode materials, as protective coatings for electrodes and as electrodes for the selective deposition of metal ions. The main application of these polymers is, however, in liquid crystals.

The thiophene derivatives of the present
30 invention may also be co-polymerised with other monomers, for example with pyrrole, thiophene, styrene, N-vinylcarbazole or any other monomer with which it will copolymerise. These copolymers are also included within the scope of the invention.

35 The present invention will be further described with reference to the following Examples.

EXAMPLE 1

5 Preparation of 4-cyano-4'-(3-thienyloxyethoxymethyl)-
biphenyl

(A) Preparation of 4-cyano-4'-bromomethylbiphenyl

10 4-cyano-4'-methylbiphenyl (1g, 0.005 mol) was
added to refluxing tetrachloromethane solution of
N-bromosuccinimide (1.1g, 0.006 mol) and
azobisisobutyronitrile (50 mg). The solution was
refluxed for four hours, allowed to cool and filtered
to leave a yellow solution. The solvent was removed
15 by evaporation to give a yellow solid which was
recrystallised from a mixture of diethyl ether/hexane
(yield 43%). δ H(CDCl₃) 7.25-7.72 (8H,m), 4.53
(2H,s).

20 (B) Preparation of 4-cyano-4'-(3-O-thienylethoxy-
methoxy)biphenyl

Sodium hydride (60% by weight) was activated
with hexane in a Schlenck tube and a solution of
25 3-(hydroxyethoxy)thiophene (1.0g) in dry
tetrahydrofuran (25 ml) was added to the Schlenck
tube. The solution was stirred for half an hour
under nitrogen and 4-cyano-4'-bromomethylbiphenyl (1
equivalent) in dry tetrahydrofuran (10 ml) was added
30 thereto.

The mixture was refluxed for 4 hours during
which time the progress of the reaction was monitored
by thin layer chromatography. The tetrahydrofuran
was evaporated and the residue dissolved in ether,
35 washed with water and dried over magnesium sulphate.
The ether was evaporated and the residue was then

chromatographed on silica to give 4-cyano-4'-(3-thienyloxyethoxymethyl)biphenyl (yield 10%). CI m/e (Intensity %): 336 (100, M + 1);

5 δ H(CDCl₃) 7.45-7.71 (8H, m), 6.25-7.18 (3H, m), 4.67 (2H, s), 3.83-4.17 (4H, m); δ C(CDCl₃) 68.5, 69.4, 72.6, 97.4, 110.6, 118.8, 119.4, 124.6, 127.1, 127.4, 128.2, 132.4, 138.2, 138.5, 145.0, 157.0.

10

EXAMPLE 2

Preparation of 4-cyano-4'-(3-thienylmethoxy)biphenyl

(A) Preparation of 4-cyano-4'-hydroxybiphenyl

15

4-cyano-4'-methoxybiphenyl (5.0g) was added to a suspension of sodium ethanethiolate (4 equivalents) in dry dimethylformamide (150 ml). The suspension was refluxed for 2 hours and then allowed to cool. Hydrochloric acid (1M) was added dropwise until the pH was 7 and the suspension extracted with diethyl ether (3 X 100 ml). The ether was evaporated to leave a white solid which was used in the next step without further purification (yield 80%).

20

25

δ H(CDCl₃) 8.74 (1H, s), 7.80 (4H, s), 7.00, 7.61 (4H, dd).

(B) Preparation of 4-cyano-4'-(3-thienylmethoxy)-biphenyl

30

4-cyano-4'-hydroxybiphenyl (4.8g, 0.025 mol) was refluxed with finely divided sodium metal (1 equivalent) for 18 hours until the sodium had completely reacted. The reaction mixture was cooled to room temperature, tetrahydrofuran (90 ml) and 3-bromomethylthiophene (4.43g, 0.025 mol) were added

35

EXAMPLE 4

Properties of 4-cyano-4'-(3-thienylmethoxy)biphenyl and its polymers

5

A differential scanning calorimeter trace for 4-cyano-4'-(3-thienylmethoxy)biphenyl is shown in Figures 1, 2a and 2b. On warming there is a transition at 157.8°C and a very weak transition at about 166°C. The cooling cycle shows a hysteresis with a major peak at 131.5°C, a shoulder at about 130°C and some minor peaks between 100°C and 127.5°C.

15 A differential scanning calorimeter trace for the polymer of 4-cyano-4'-(3-thienylmethoxy)biphenyl with tetrafluoroborate counterions is shown in Figure 3a for the heating cycle and in Figure 3b for the cooling cycle. In the heating cycle there is a shoulder at 76.7°C and a transition peak at 111.3°C on the first heating cycle, but no transitions were observed in the cooling cycle.

20 Thermal cycling of this polymer below 130°C shows transitions in both the heating and cooling cycles and these are shown in Figures 4a and 4b. This material thus has liquid crystal properties below 130°C.

25 Cyclic voltammetry of 4-cyano-4'-(3-thienylmethoxy)biphenyl (5 mmol) was carried out at a platinum electrode in acetonitrile with tetrabutylammonium perchlorate (0.5 M) as the supporting electrolyte in the voltage range of -2.0V to +1.5V versus an Ag/AgCl electrode. The cyclic voltammograms are shown in Figure 5.

EXAMPLE 5

Liquid crystal properties of 4-cyano-4'-(3-thienylmethoxy)biphenyl

5

Homogeneous (parallel) alignments of 4-cyano-4'-(3-thienylmethoxy)biphenyl in a chloroform solution were effected on an indium-tin oxide electrode in a conventional manner. A sandwich cell was then constructed using another indium-tin-oxide electrode pressed against the coated electrode with transparent tape.

A blue light was emitted for the homogeneously aligned 4-cyano-4'-(3-thienylmethoxy)biphenyl at a current density of 22 mA cm⁻².

EXAMPLE 6

Liquid crystal properties of 4-cyano-4'-(3-thienylmethoxy)biphenyl

20

Solutions of 2.6% and 5.2% by weight of 4-cyano-4'-(3-thienylmethoxy)biphenyl in a eutectic mixture of cyanobiphenyls known as E7 (from BDH, Poole, Dorset) were prepared.

25

The following properties were observed:

Clearing Point

°C

30

E7	57.9
2.6% solution	59.0
5.2% solution	59.8
Extrapolated	93.9

35

for 4-cyano-4'-(3-thienylmethoxy)biphenyl

Birefringence

		n_o	n_e
5	E7	1.52254	1.74569
	2.6% solution	1.52333	1.75097
	5.2% solution	1.52384	1.75322
	Extrapolated	1.54759	1.89100
10	for 4-cyano-4'-(3-thienylmethoxy)biphenyl		

$$n=0.34341$$

Viscosity

15		m^2/s
	E7	40.5×10^{-6}
	2.6% solution	41.9×10^{-6}
20	5.2% solution	43.8×10^{-6}
	Extrapolated	182.4×10^{-6}
	for 4-cyano-4'-(3-thienylmethoxy)biphenyl	

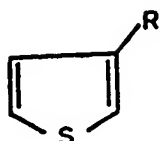
25 Dielectric Anisotropy

	E7	17.08	5.01	12.07
	2.5% solution	17.38	5.02	12.36
	5.0% solution	18.01	5.06	12.95
30	Extrapolated			29.62
	for 4-cyano-4'-(3-thienylmethoxy)biphenyl			

CLAIMS:

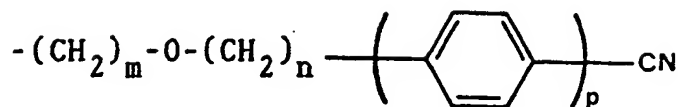
1. A compound having the general formula

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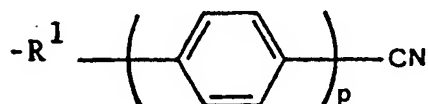
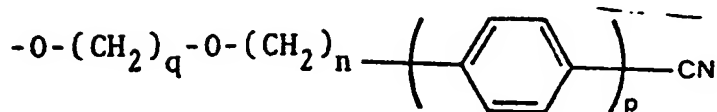


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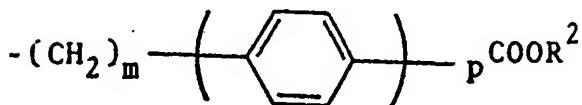
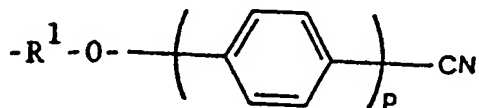
10 wherein R is



15



20



25

R^1 is a straight or branched chain alkylene group containing from 1 to 8 carbon atoms;

R^2 is a phenyl group substituted with a cyano group or an alkoxy group containing from 1 to 6 carbon atoms;

30

n is 0 or an integer of from 1 to 6;

m is 0 or an integer of from 1 to 6;

35

p is an integer of from 1 to 3;

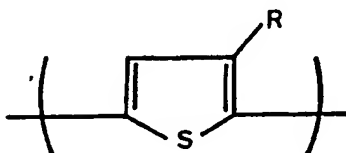
q is an integer of from 1 to 6.

2. 4-cyano-4'-(3-thienyloxyethoxymethyl)-biphenyl.

5 3. 4-cyano-4'-(3-thienylmethoxy)biphenyl.

4. A polythiophene derivative which comprises repeating units of the general formula:

10



15 wherein R is as defined above, and counterions of the formula X, where X is chloride, bromide, sulphate, bisulphate, nitrate, tetrafluoroborate, alkylsulphonate, arylsulphonate, arenecarboxylate, alkylcarboxylate, arenedicarboxylate, polystyrene-sulphonate, polyacrylate, cellulose sulphonate, cellulose sulphate, polyamic carboxylate, H_2PO_3^- , H_2PO_4^- , PF_6^- , SbF_6^- , AsF_6^- or a perfluorinated polyanion.

25 5. A process for the preparation of a polythiophene derivative as claimed in claim 4 which process comprises subjecting a thiophene monomer as above defined in a non-aqueous solvent to electrochemical oxidation at an electrode potential
30 which is at least as electropositive as the oxidation potential of the thiophene monomer.

35 6. A process as claimed in claim 5 wherein the solvent is acetonitrile, dichloromethane, chloroform, nitromethane, dichloroethane, nitrobenzene, propylene carbonate, N-methylpyrrolidone, sulpholane,

dimethylformamide, dimethylsulphoxide or a mixture of two or more thereof.

7. A process as claimed in claim 5 or claim 6
5 wherein the electrochemical oxidation is carried out in an electrolyte which provides the counterions X, where X is as defined in claim 5.

8. A copolymer of a compound as claimed in any
10 one of claims 1 to 3 with a monomer which is polymerisable therewith

9. The use of a compound as claimed in any one of claims 1 to 3, or of a polymer as claimed in claim
15 4, or of a copolymer as claimed in claim 8, in a liquid crystal.

20

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